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(54) **Cosmetics with enhanced adherence to the skin.**

(57) A method of enhancing adherence to the skin of a skin care preparation containing an active ingredient by incorporating into the skin care preparation a film forming agent as an ingredient and applying the skin care preparation containing the active ingredient and the film forming agent to the skin. The invention is characterized by the film forming agent being an aqueous latex of a crosslinked polydiorganosiloxane. Sunscreen preparations and eye cosmetics are described.

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This invention is directed to personal care and, more particularly, to skin care products including color cosmetics, which have been found to possess improved skin substantivity characteristics.

Water and wear resistance are vital properties to skin protection products, since contact with water by perspiration and swimming, can destroy the effectiveness of an otherwise beneficial skin care product. Where greater protective qualities, high water resistance and substantive barrier characteristics, are desired in a skin care product, it is customary in the art to incorporate various organic waxes, organic resins and organic polymers, into the skin care product in order to achieve these goals.

What has been discovered in accordance with the present invention is that certain silicone based materials can be employed as viable alternatives to the organic waxes, resins and polymers, customarily used heretofore. Specifically, the silicone based material is an aqueous latex of a crosslinked polydiorganosiloxane.

While the aqueous latex of the crosslinked polydiorganosiloxane is described in U.S. Patent No. 4,584,341 issued April 22, 1986, the use of the aqueous latex of the '341 patent in the manner set forth in accordance with the present invention, has not been previously exploited. Thus, insofar as the '341 patent is concerned, the use of the aqueous latex therein is described with reference to (i) coatings and impregnants for paper or fabric products, (ii) construction coatings, (iii) film cast products, (iv) thick cast parts, (v) caulking and (vi) electrically conductive films.

There is no suggestion in the '341 patent that the aqueous latex compositions described therein would possess utility in the personal care arena.

The invention relates to a method of enhancing the adherence to the skin of a skin care preparation containing an active ingredient such as a pigment, sunscreen, moisturizer or emollient. The method involves incorporating into the skin care preparation a film forming agent as an ingredient thereof and applying the skin care preparation containing the active ingredient and the film forming agent to the skin. The film forming agent according to the present invention is an aqueous latex of a crosslinked polydiorganosiloxane.

The invention further relates to a sunscreen preparation containing a film forming agent and at least one ultraviolet light absorbing compound as an active ingredient. The invention is characterized by the use of an aqueous latex of a crosslinked polydiorganosiloxane as the film forming agent in the sunscreen preparation.

In addition, the invention relates to an eye cosmetic containing a film forming agent, a pigment, a wax, an oil and a preservative. Again, an aqueous latex of a crosslinked polydiorganosiloxane is used as the film forming agent in the eye cosmetic. Where the active ingredient is a pigment for example, the pigment is caused to be adhered to the eyelashes in accordance with the present invention.

The film forming agent of the present invention can be best described as an aqueous latex of a crosslinked polydiorganosiloxane prepared by a method comprising

(A) homogenizing a mixture comprising (1) one hundred parts by weight of polydiorganosiloxane of the formula  $\text{HO}(\text{R}_2\text{SiO})_x\text{H}$  wherein R is a radical selected from methyl, ethyl, propyl, phenyl, vinyl, allyl and 3,3,3-trifluoropropyl and x is an integer having an average value of three to one hundred; (2) 15-75 millimoles of surface active anionic catalyst per kilogram of polydiorganosiloxane wherein said catalyst is selected from dodecylbenzene sulfonic acid and hydrogen lauryl sulfate; and (3) water, to yield an oil in water emulsion;

(B) admixing 0.5-15 parts by weight of an alkoxy silicon compound selected from (i) silanes of the formula  $\text{R}'_3\text{Si}(\text{OR}^3)_4$  wherein R' is a monovalent hydrocarbon radical having up to twelve carbon atoms, R<sup>3</sup> is an alkyl radical having one to six carbon atoms and a has a value of zero or one; (ii) a partial hydrolyzate of the silane which is soluble in the polydiorganosiloxane; and (iii) mixtures of the silane and the partial hydrolyzate;

(C) maintaining the emulsion at a temperature of 15 to 30°C. for at least five hours at a pH of less than five until a crosslinked polymer emulsion is formed;

(D) admixing sufficient base to raise the pH of the crosslinked polymer emulsion to greater than seven; and optionally

(E) admixing greater than one part by weight of colloidal silica sol or colloidal silsesquioxane; to yield a latex which produces an elastomer upon removal of the water at room temperature.

Details of the aqueous latex and examples of a process for its manufacture are set forth in U.S. Patent No. 4,584,341. The aqueous latex is also available commercially from Dow Corning Corporation, Midland, Michigan, USA.

For the purpose of illustrating the present invention in more detail, oil in water emulsion mascara compositions B-H were prepared containing the aqueous latex and these compositions are set forth in Table I. Mascara composition H was used as the control mascara. The various ingredients of the mascara compositions are arranged as Groups A-E as indicated in Table I.

TABLE I

## MASCARA COMPOSITIONS (WEIGHT %)

INGREDIENTS	B	C	D	E	F	G	H
Group A:							
1. Water	47.5	57.5	57.5	57.5	47.5	47.5	57.5
2. Magnesium Aluminum Silicate	1.5	1.5	1.5	1.5	1.5	1.5	1.5
3. Triethanolamine	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Group B:							
4. Black Iron Oxide	10.0	10.0	10.0	10.0	10.0	10.0	10.0
5. Ultramarine Blue	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Group C:							
6. Carnauba Wax	2.0	2.0	2.0	2.0	2.0	2.0	2.0
7. Candelilla Wax	5.0	5.0	5.0	5.0	5.0	5.0	5.0
8. Stearic Acid	4.0	4.0	4.0	4.0	4.0	4.0	4.0
9. Beeswax	5.0	-	-	-	5.0	5.0	5.0
10. Petroleum Distillate (ISOPAR®)	10.0	10.0	10.0	10.0	10.0	10.0	10.0
11A. Alkylmethyl Silicone Wax with C <sub>30</sub> + alkyl group	-	5.0	-	-	-	-	-
11B. Same as 11A but shorter silicone backbone	-	-	5.0	-	-	-	-
11C. Same as 11A but with C <sub>22-24</sub> alkyl group	-	-	-	5.0	-	-	-
Group D:							
12A. Aqueous Silicone Latex	10.0	-	-	-	-	-	-
12B. Silicone Pressure Sensitive Adhesive	-	-	-	-	10.0	-	-
12C. High Molecular Weight Silicone Gum HOMe <sub>2</sub> SiO(Me <sub>2</sub> SiO) <sub>n</sub> SiMe <sub>2</sub> OH	-	-	-	-	-	10.0	-
Group E:							
13. Diazolidinyl urea (Germaben® II-E)	1.0	1.0	1.0	1.0	1.0	1.0	1.0

In Table I, ingredient 2 of Group A is a thickener sold under the trademark VEEGUM® by R.T. Vanderbilt Co. Inc., of Norwalk, Connecticut. The petroleum distillate shown as ingredient 10 of Group C is a mixture of isoparaffins containing hydrocarbons having ten to twelve carbon atoms, sold under the trademark ISOPAR® L by the Exxon Chemical Company, Houston, Texas. The preservative GERMABEN® II-E shown as ingredient 13 in Group E, is a product and a trademark of Sutton Laboratories of Chatham, New Jersey.

The aqueous latex of crosslinked polydiorganosiloxane used as the film forming agent in the mascara compositions in Table I appears in Group D as ingredient 12A.

In Table I, an "in situ" emulsifier is employed in the form of the compound triethanolamine stearate which is formed by the combination of triethanolamine (Ingredient 3) and stearic acid (Ingredient 8).

Example I

Mascara compositions B-H in the form of oil in water emulsions were prepared by heating ingredient 1 and adding ingredients 2 and 3, in that order. The mixture of ingredients 1-3 was covered and heated to 85°C. The pigment ingredients 4 and 5 of Group B were added to the ingredients 1-3 of Group A and dispersed using a homomixer. The ingredients of Groups A and B were maintained at 85°C. All of the ingredients of Group C were heated together to 80°C. and added to Groups A and B using a propeller mixer. Groups A, B and C, were mixed at 80°C. for fifteen minutes, cooled to 50°C. and the ingredients of Group D were added. Groups A, B, C and D, were cooled to 35°C. and the preservative of Group E was added. The mascara compositions were filled into vials and evaluated in Examples II and III.

Example II

The mascara compositions in Table I were evaluated for shelf stability and found to be stable at temperatures of 40 and 45°C. after a period of six months.

Example III

Mascara compositions B-H in Table I were evaluated in vivo by volunteers. The volunteers applied the mascara compositions to their eyelashes and attempted to wash off the mascara. Each mascara composition was evaluated on the basis of its difficulty to wash off the eye lashes. The volunteers reported that mascara composition B which is representative of the present invention, was the most difficult to wash off, followed by mascara compositions D and G.

In the tests, Composition B was evaluated against other compositions containing other types of silicone film forming materials shown as ingredients 11A-11C, 12B and 12C, in Table I. Ingredient 11A was an alkyl-methyl functional silicone wax containing an alkyl group of thirty carbon atoms. Ingredient 11B was an alkyl-methyl functional silicone wax containing an alkyl group of thirty carbon atoms and differed from silicone wax 11A only in the length of the siloxane backbone. The siloxane backbone of wax 11B was shorter than the siloxane backbone of wax 11A. Ingredient 11C was also an alkylmethyl functional silicone wax similar to silicone wax 11A, but wax 11C contained an alkyl group of 22-24 carbon atoms. Film forming silicone Ingredient 12B was a medical grade silicone pressure sensitive adhesive. Ingredient 12C was a high molecular weight silicone gum having the formula  $\text{HOMe}_2\text{SiO}(\text{Me}_2\text{SiO})_n\text{SiMe}_2\text{OH}$  in which Me is methyl and n is an integer having a value of ten thousand.

The testing results reported by the volunteers were confirmed by independent testing of mascara composition B against other mascaras containing organic film forming agents such as polyvinylpyrrolidone and acrylate based polymers.

While Examples I-III and Table I are directed to mascara compositions in the form of oil in water emulsions, water in oil emulsions may be formulated as well. Further, the aqueous latex of crosslinked polydiorganosiloxane may be used in the preparation of other eye cosmetic preparations such as eyebrow pencils and liquids, eye shadow, eyeliner and eye cream. In addition, it is contemplated that mascara compositions containing the aqueous latex as the film forming agent may be formulated as cake or block mascara, liquid mascara or cream mascara, products.

Waxes which may be employed in preparing mascara compositions in accordance with the present invention include carnauba, beeswax, ceresin, paraffin, candelilla, bayberry, montan, spermaceti, castor wax, ozokerite, Fisher-Tropsch waxes and microcrystalline waxes. Suitable oils include castor oil, olive oil, jojoba oil, stearic acid, lanolin alcohols, paraffin oil and silicone fluids. Examples of pigments include iron oxide, titanium oxide, ultramarine, chromium oxide, carbon black and any of the United States Government Food & Drug Administration (FDA) certified organic dyes and lakes. Preservatives include methyl paraben, propyl paraben, butyl paraben, diazolidinyl urea and imidazolidinyl urea.

It may be desirable to incorporate in the mascara composition other conventional ingredients such as emulsifiers and surfactants; humectants such as glycerine; perfumes, sunscreen compounds; vitamins; hormones; amino acids; antioxidants such as propyl, octyl and dodecyl, esters of gallic acid, butylated hydroxyanisole, butylated hydroxytoluene and nordihydroguaiaretic acid; extenders such as talc, mica, kaolin and cericite; feel modifiers such as organic esters and silicone fluids; opacifiers such as titanium dioxide and fatty alcohols; fragrances; and solvents such as ethanol, isopropanol and volatile silicones such as hexamethyldisiloxane and octamethylcyclotetrasiloxane.

A mascara formulation in accordance with the present invention will preferably contain 5-20 percent by weight or most preferably ten percent by weight, of the aqueous latex of crosslinked polydiorganosiloxane; 20-

60 percent by weight or most preferably 30-50 percent by weight, of water; 4-10 percent by weight of a wax or a mixture of waxes; 10-20 percent by weight of one or more pigments; one percent by weight or less of a preservative; 5-15 percent by weight of one or more surfactants or emulsifiers; 0.2-3.0 percent by weight of a thickener; zero to one percent by weight of a feel modifier; and 1-4 percent by weight of an opacifier.

The concept of the present invention is further illustrated by reference to Table II which shows five (5) sunscreen compositions A-E which were prepared. The various ingredients of the sunscreen compositions A-E are grouped as Phases A, B and C. Ingredients in Table II which correspond to ingredients in Table I above are similarly identified. Any differences are noted below.

TABLE II

SUNSCREEN COMPOSITIONS  
(WEIGHT PERCENT)

<u>INGREDIENTS</u>		A	B	C	D	E
PHASE A:						
1. Water		68.21	63.21	70.71	68.57	70.71
2. Polyacrylate (CARBOPOL®940)		0.14	0.14	0.14	0.14	0.14
3. GLYCERIN		2.50	2.50	2.50	2.50	2.50
4. Methyl Paraben		0.15	0.15	0.15	0.15	0.15
5. Triethanolamine		1.40	1.40	1.40	1.40	1.40
PHASE B:						
6. Stearic Acid		4.00	4.00	4.00	4.00	4.00
7. Cetyl Alcohol		1.00	1.00	1.00	1.00	1.00
8. DEA-Cetyl Phosphate (AMPHISOL)		1.00	1.00	1.00	1.00	1.00
9. Propyl Paraben		0.10	0.10	0.10	0.10	0.10
PHASE C:						
10. C <sub>12</sub> -C <sub>15</sub> Alkylbenzoate (FINSOLV®TN)		4.00	4.00	4.00	4.00	4.00
11. 2-ethylhexyl-p- methoxycinnamate PARSOL®MCX		7.00	7.00	7.00	7.00	7.00
12. 2-hydroxy-4- methoxybenzophenone UVINUL® H-40		3.00	5.00	3.00	3.00	3.00
13A. Silicone Pressure Sensitive Adhesive		7.50	-	-	-	-
13B. Acrylates Polymer POLYTRAP®		-	12.50	-	-	-
13C. Silicone Polymer		-	-	5.00	-	-
13D. Crosslinked Cationic Emulsion of Polydimethylsiloxane		-	-	-	7.14	-
13E. Aqueous Silicone Latex		-	-	-	-	5.00

In Table II, the polyacrylate thickener CARBOPOL® 940 in Phase A is a product and trademark of the B.F. Goodrich Company of Cleveland, Ohio. Glycerin was present in Phase A as a humectant. The emulsifier AMPHISOL® in Phase B is a trademark and a product of Givaudan Corporation, Clifton, New Jersey. Cetyl alcohol

was present in Phase B as an opacifier. The solubilizer FINSOLV® TN in Phase C is a product and a trademark of Finetex Incorporated of Elmwood Park, New Jersey. The sunscreen compound PARSOL® MCX in Phase C is a product and a trademark of Givaudan Corporation of Clifton, New Jersey. The sunscreen compound UVINUL® M-40 in Phase C is a product and a trademark of BASF Corporation of Parsippany, New Jersey.

5 The acrylates polymer PPLYTRAP® in Phase C is a product and trademark of the Dow Corning Corporation, Midland, Michigan. POLYTRAP® is a micrometer sized powder of macroporous particulates and is described in various patents including U.S. Reissue Patent 33429 and U.S. Patent No. 5,035,890. The silicone polymer 13C was a dimethylvinyl endblocked trifluoropropylmethyl siloxane polymer. The silicone ingredient 13D was a water thin white emulsion which had a silicone content of thirty-five percent by weight in water and  
10 a pH of six.

#### Example IV

Sunscreen compositions A-E in Table II were prepared by mixing together the ingredients of Phase A and  
15 heating the mixture to 76°C. The ingredients of Phase B were mixed together in order and heated to 75°C. Phase B was added to Phase A and the temperature was maintained. Ingredients 10-12 of Phase C were mixed together in order and heated until dissolved. This portion of Phase C was added to ingredient 13A-E as appropriate and all of Phase C was added to Phases A and B at 50°C. The sunscreen compositions were stirred until a temperature of 40°C. was reached and filled into vials for evaluation.

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#### Example V

Sunscreen compositions A-E were evaluated *in vivo* by volunteers. The amount of sunscreen composition remaining on the skin after eighty minutes of soaking was determined by Fourier-Transform Infrared Spectroscopy (FTIR). The sunscreen compositions A-E were evaluated against a commercial sunscreen product containing a GANEX® resin as the film forming agent. GANEX® is a polyvinylpyrrolidone based polymer  
25 commonly used in consumer sunscreen products and is a product and trademark of International Specialty Products of Wayne, New Jersey. It was determined that the sunscreen composition E of the present invention was the best performer against GANEX®. Slightly more than forty percent of the sunscreen composition E which contained the aqueous latex remained on the skin. By comparison, only thirty percent of the sunscreen containing GANEX® as the film forming agent remained on the skin.

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Sunscreen compositions according to the present invention may be formulated as oils, lotions, creams or gels. In those instances where a composition is in the form of an oil in water emulsion or a water in oil emulsion, one or more surfactants may be required. Suitable surfactants would include one or more of the various categories of silicon-free organic emulsifiers. These emulsifiers, it is noted, may be used in combination with certain polydiorganosiloxanepolyoxyalkylene copolymers, as explained in U.S. Patent No. 4,122,029 and U.S. Patent No. 4,311,695.

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Sunscreen agents according to the invention are used in amounts which are within the restricted limits or less, as established by the US Government Food & Drug Administration. Representative sunscreen agents or mixtures of such agents which may be used in the preparation of the compositions of the invention include  
40 4-aminobenzoic acid; homomethyl salicylate; 2-hydroxy-4-methoxy benzophenone; 2-phenylbenzimidazol-5-sulfonic acid; 4-dimethyl amino benzoic acid-2-ethylhexyl ester; 4-methoxy cinnamic acid isoamyl ester; 4-methoxy cinnamic acid-2-ethylhexyl ester; 3-(4'-methyl) benzylidene-bornane-2-one; 1-(4'-isopropylphenyl)-3-phenyl-1-propane-1,3-dione; and 1-(4'-t-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione.

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Among the various moisturizing oils which may be used in order to formulate sunscreen compositions are mineral oil, peanut oil, sesame oil, avocado oil, coconut oil, cocoa butter, almond oil, safflower oil, corn oil and cotton seed oil. Other oils may be added for the purpose of improving the spreadability of the sunscreen composition such as silicone fluids; and fatty acid esters such as isopropyl myristate, isopropyl palmitate, isopropyl stearate, butyl stearate and cetyl stearate. Other conventional adjuvants necessary to produce acceptable consumer sunscreen products may be included in the compositions such as antioxidants, preservatives,  
50 fragrances and perfumes, emulsifiers, humectants and solvents.

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A sunscreen formulation in accordance with the present invention will preferably contain 5-20 percent by weight or most preferably ten percent by weight, of the aqueous latex of crosslinked polydiorganosiloxane; 20-60 percent by weight or most preferably 30-50 percent by weight, of water; one percent by weight or less of a preservative; 4-8 percent by weight of one or more surfactants or emulsifiers; 0.1-2.0 percent by weight of a thickener; zero to five percent by weight of a feel modifier; 0.2-1.0 percent by weight of a fragrance; and 1-4 percent by weight of an opacifier.

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The use of the aqueous silicone latex in the preparation of foundation make-up is illustrated in the following

example. In the example, three foundation make-ups A, B and C, were prepared and the formulation for each of these foundation make-ups is shown in Table III. Foundation make-ups B and C contained the aqueous silicone latex, while foundation make-up A was used as the control.

In Table III, SPAN® 60 is a nonionic emulsifier with an HLB value of 4.7. It is a sorbitan monostearate and a product of ICI Americas Incorporated, of Wilmington, Delaware. CERASYNT® Q in Table III is an anionic emulsifier and a glycerol monostearate. It is a product of Van Dyk of Belleville, New Jersey. The nonionic emulsifier LIPONIC® EG-1 is a polyethoxylated glycerol and a product of Lipo Chemical Incorporated of Paterson, New Jersey.

The pigment grind in Table III may contain one or more pigments such as iron oxides, talcum, titanium dioxide, ultramarines (pink, rose and blue), chromium green, manganese violet, kaolin, bentonite, silica, zinc oxide and chromic oxide.

#### Example VI

Referring to Table III, foundation make-ups A-C were prepared by mixing the several ingredients in Phase A in the order given in the Table. The pigment grind was added to Phase A using a homomixer for providing agitation. Heat was applied to Phases A and B and Phase C was heated separately. Phases A-C were combined and Phase D was added. The foundation make-up was cooled and evaluated by volunteers.

The foundation make-ups were tested "in vivo" by applying 0.05 milliliters to the volar forearm of the volunteers. After being applied, the foundation make-up was allowed to dry for ten minutes. Luke warm tap water was applied to each application site for two minutes. The forearm was then evaluated to determine how much foundation remained on the skin. These evaluations confirmed that foundation make-ups B and C of the present invention were more resistant to water wash off than foundation make-up A which did not contain the aqueous silicone latex.

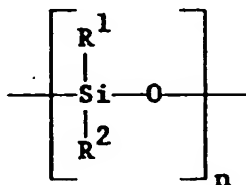
The volunteers were also asked to evaluate the test site for removal of the foundation make-up with a tissue by rubbing. It was reported that all of the foundation make-ups A-C could be removed by rubbing with tissues, but that foundation make-ups B and C of the present invention retained more color than foundation make-up A which did not contain the aqueous silicone latex.

TABLE III

INGREDIENTS		FOUNDATION MAKE-UP (WEIGHT %)		
		A	B	C
PHASE A:				
1.	Water	62.55	57.55	52.55
2.	Magnesium aluminum silicate	1.00	1.00	1.00
3.	PEG - 400	5.00	5.00	5.00
4.	LIPONIC EG-1	5.00	5.00	5.00
5.	Triethanolamine	0.20	0.20	0.20
PHASE B:				
6.	Pigment Grind	10.00	10.00	10.00
PHASE C:				
7.	CERAPHYL 140A	2.00	2.00	2.00
8.	CERASYNT Q	1.00	1.00	1.00
9.	SPAN 60	1.75	1.75	1.75
10.	Stearic Acid	0.50	0.50	0.50
11.	Volatile cyclic silicone	10.00	10.00	10.00
PHASE D:				
12.	Aqueous Silicone Latex	—	5.00	5.00
13.	GERMABEN® II-E	1.00	1.00	1.00

The cosmetic compositions set forth above in Tables I to III and in Examples I to VI, when applied to the skin, leave a flexible and stretchable film on the surface of the skin. Therefore, active ingredients included in these cosmetic products such as sunscreen compounds for example, will tend to be bound in the flexible film and will remain in place on the skin significantly longer, despite sweating, swimming and exercise. Further, the compositions exhibit improved physical resistance and hence are physically difficult to rub off from the skin. These obvious advantages of the compositions according to the present invention can be attributed to the presence in the compositions of the aqueous latex of the crosslinked polydiorganosiloxane.

Non-volatile silicone fluids which may be used in the preparation of the compositions of the present invention are organic polysiloxanes having a viscosity in the range of 5 to as high as several million mm<sup>2</sup>/s (centistokes), preferably 100 to 10,000 mm<sup>2</sup>/s (centistokes). A mixture of polysiloxanes having relatively higher and relatively lower viscosities can be employed. Such polysiloxanes have the repeating unit



wherein n is an integer having a value greater than 1; R<sup>1</sup> and R<sup>2</sup> are alkyl radicals of one to seven carbon atoms or a phenyl group; and R<sup>1</sup> and R<sup>2</sup> may be the same or different. Illustrative polysiloxanes are polydimethylsi-



loxane, polydiethylsiloxane, polymethylethylsiloxane, polymethylphenylsiloxane, polydiphenylsiloxanes and copolymers of two or more of the foregoing siloxanes.

In some instances it may be desirable to include a volatile silicone fluid in the compositions of the present invention. Suitable volatile silicones are low viscosity methylsilicones. The volatile low viscosity methylsilicone fluid corresponds to the average unit formula  $(\text{CH}_3)_a\text{SiO}_{(4-a)/2}$  wherein  $a$  is an integer having an average value of from two to three. The methylsilicone fluid contains siloxane units joined by Si-O-Si bonds. Representative units are  $(\text{CH}_3)_3\text{SiO}_{1/2}$ ,  $(\text{CH}_3)_2\text{SiO}_{3/2}$ ,  $(\text{CH}_3)\text{SiO}_{5/2}$  and  $\text{SiO}_{7/2}$ . These units are present in molar amounts such that there is provided an average of from two to three methyl groups per silicon atom in the methylsilicone fluid, whereby the methylsilicone fluid has a viscosity of less than one hundred mm<sup>2</sup>/s (centistokes) measured at 25°C.

The volatile, low viscosity methylsilicone fluid contains dimethylsiloxane units and optionally trimethylsiloxane units. Preferably, the methylsilicone fluid has a viscosity of less than ten mm<sup>2</sup>/s (centistokes). Representative compounds are cyclopolyxiloxane compounds of the general formula  $[(\text{CH}_3)_2\text{SiO}]_x$  and linear siloxane compounds of the general formula  $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_y\text{Si}(\text{CH}_3)_3$ , in which  $x$  is an integer having a value of from three to ten and  $y$  is an integer having a value of from zero to four.

The volatile, low viscosity methylsilicones have boiling points generally less than 250°C. and possess viscosities preferably generally less than ten mm<sup>2</sup>/s (centistokes) measured at 25°C. Most preferably, the viscosity is 0.65 to 5.0 mm<sup>2</sup>/s (centistokes). The cyclopolyxiloxane compounds have been assigned the adopted name "CYCLOMETHICONE" by The Cosmetics, Toiletries and Fragrance Association, Inc., Washington, D.C. (CTFA). Both the cyclopolyxiloxanes and the linear siloxanes are clear fluids and are essentially odorless, non-toxic, nongreasy and nonstinging. Cosmetically, these methylsilicone fluids are nonirritating to skin and exhibit enhanced spreadability and ease of rub-out when applied. Once applied, the materials evaporate leaving behind no residue.

Methylsilicone fluids which are operable in accordance with the present invention leave substantially no residue after thirty minutes at room temperature when one gram of fluid is placed at the center of a No. 1 circular filter paper having a diameter of 185 mm supported at its perimeter in open room atmosphere. By methylsilicone fluid is meant a composition containing two or more silicon atoms, all of which are bonded by way of at least one oxygen atom to at least one other silicon atom and at least one methyl radical, each silicon valence not satisfied by oxygen being satisfied by a methyl radical.

Representative methylsilicone fluids found to be especially useful in accordance with the present invention are hexamethyldisiloxane which has a boiling point of 99.5°C. and the formula  $\text{Me}_6\text{Si}_2\text{O}$ ; octamethyltrisiloxane which has a boiling point of 152°C. and the formula  $\text{Me}_8\text{Si}_3\text{O}_2$ ; hexamethylcyclotrisiloxane which has a boiling point of 133°C. and the formula  $[(\text{Me}_2)\text{SiO}]_3$ ; octamethylcyclotetrasiloxane which has a boiling point of 171°C. and the formula  $[(\text{Me}_2)\text{SiO}]_4$ ; and decamethylcyclopentasiloxane which has a boiling point of 205°C. and the formula  $[(\text{Me}_2)\text{SiO}]_5$ .

These methylsilicone fluids may be used alone or as mixtures in combinations of two or more. Mixtures of the methylsilicone fluids will result in a volatile material having an evaporating behavior different from any one of the individual methylsilicone fluids. The methylsilicone fluids and methods for their preparation are known in the art and such fluids are commercially available.

In some instances, it may be desirable to replace one or more of the methyl groups in the methylsilicone fluid with other groups. Thus, there may be substituted groups such as alkyl radicals having two to twelve carbon atoms; aryl radicals having six to ten carbon atoms; amine groups; vinyl; hydroxyl; haloalkyl groups; aralkyl groups; and acrylate groups, for example.

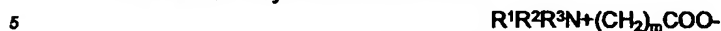
The compositions of this invention may contain a surfactant such as an anionic and amphoteric surfactant. Suitable anionic surfactants include sulfonated and sulfated alkyl, aralkyl and alkaryl anionic surfactants; alkyl succinates; alkyl sulfosuccinates and N-alkyl sarcosinates. Representative surfactants are the sodium, magnesium, ammonium and the mono-, di- and triethanolamine salts of alkyl and aralkyl sulfates as well as the salts of alkaryl sulfonates. The alkyl groups of the surfactants generally have a total of from 12 to 21 carbon atoms, may be unsaturated and are preferably fatty alkyl groups. The sulfates may be sulfate ethers containing one to ten ethylene oxide or propylene oxide units per molecule. Preferably, the sulfate ethers contain 2 to 3 ethylene oxide units.

Typical anionic surfactants include, among others, sodium lauryl sulfate, sodium lauryl ether sulfate, ammonium lauryl sulfate, triethanolamine lauryl sulfate, sodium C14-16 olefin sulfonate, ammonium pareth-25 sulfate (ammonium salt of a sulfated polyethylene glycol ether of a mixture of synthetic C12-15 fatty alcohols), sodium myristyl ether sulfate, ammonium lauryl ether sulfate, disodium monooleamidossulfosuccinate, ammonium lauryl sulfosuccinate, sodium dodecylbenzene sulfonate, triethanolamine dodecylbenzene sulfonate and sodium N-lauroyl sarcosinate.

Surfactants generally classified as amphoteric or ampholytic include cocoamphocarboxyglycinate, co-

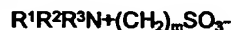
coamphocarboxypropionate, cocobetaine, N-cocamidopropyl dimethylglycine and N-lauryl-N-carboxymethyl-N-(2-hydroxyethyl)ethylenediamine. Other suitable amphoteric surfactants include the quaternary cycloimidates, betaines and sultaines disclosed in U.S. Patent No. 3,964,500.

The betaines may have the structure:



wherein  $R^1$  is an alkyl group having 12 to 18 carbon atoms or a mixture thereof,  $R^2$  and  $R^3$  are independently lower alkyl groups having 1 to 3 carbon atoms and  $m$  is an integer from 1 to 4. Specific betaines are alpha-(tetradecyldimethylammonio)acetate, beta-(hexadecyldiethylammonio)propionate and gamma-(dodecyldimethylammonio)butyrate.

The sultaines may have the structure:



wherein  $R^1$ ,  $R^2$ ,  $R^3$  and  $m$  are defined as above. Specific useful sultaines are 3-(dodecyldimethylammonio)propane-1-sulfonate and 3-(tetradecyldimethylammonio)ethane-1-sulfonate.

The compositions of this invention may contain a nonionic surfactant which is a fatty acid alkanolamide or amine oxide surfactant. The fatty acid alkanolamides are nonionic surfactants obtained by reacting alkanolamines such as monoethanolamine, diethanolamine, monoisopropanolamine or diisopropanolamine with a fatty acid or fatty acid ester to form the amide. The hydrophobic portion of the nonionic surfactant is provided by a fatty acid hydrocarbon chain which generally has from 10 to 21 carbon atoms. The fatty acid alkanolamide surfactants include, fatty acid diethanolamides such as isostearic acid diethanolamide, lauric acid diethanolamide, capric acid diethanolamide, coconut fatty acid diethanolamide, linoleic acid diethanolamides, myristic acid diethanolamide, oleic acid diethanolamide and stearic acid diethanolamide; fatty acid monoethanolamides such as coconut fatty acid monoethanolamide; and fatty acid monoisopropanolamides such as oleic acid monoisopropanolamide and lauric acid monoisopropanolamide.

The amine oxides are known nonionic surfactants obtained by oxidizing a tertiary amine to form the amine oxide. They are sometimes referred to as polar nonionic surfactants. Amine oxide surfactants include, the N-alkyl amine oxides such as N-cocodimethylamine oxide, N-lauryl dimethylamine oxide, N-myristyl dimethylamine oxide and N-stearyl dimethylamine oxide; the N-acyl amine oxides such as N-cocamidopropyl dimethylamine oxide and N-tallowamidopropyl dimethylamine oxide; and N-alkoxyalkyl amine oxides such as bis(2-hydroxyethyl) C12-15 alkoxy-propylamine oxide. The hydrophobic portion of the amine oxide surfactants is generally provided by a fatty hydrocarbon chain containing from 10 to 21 carbon atoms. Representative surfactants include lauric acid diethanolamide, N-lauryl dimethylamine oxide, coconut acid diethanolamide, myristic acid diethanolamide and oleic acid diethanolamide.

Additional categories of surfactants may be included such as cationic and zwitterionic surfactants and representative compounds are set forth in detail in U.S. Patent No. 4,902,499.

Suitable thickeners which may be employed are sodium alginate, gum arabic, polyoxyethylene, guar gum, hydroxypropyl guar gum, cellulose derivatives such as methylcellulose, methylhydroxypropylcellulose, hydroxypropylcellulose, polypropylhydroxyethylcellulose, starch and starch derivatives such as hydroxyethylamylose and starch amylose, locust bean gum, electrolytes such as sodium or ammonium chloride, saccharides such as fructose and glucose and derivatives of saccharides such as PEG-120 methyl glucose dioleate.

Other variations and modifications may be made in the compounds, compositions and methods, described herein without departing from the essential features and concepts of the present invention. The forms of the invention described herein are exemplary only and are not intended as limitations on the scope of the invention as defined in the appended claims.

## Claims

1. A method of enhancing adherence to the skin of a skin care preparation comprising an active ingredient selected from pigments, sunscreens, moisturizers and emollients, comprising the step of incorporating into the skin care preparation 5-20 percent by weight of a film forming agent as an ingredient thereof and applying the skin care preparation containing the active ingredient and the film forming agent to the skin; the film forming agent being an aqueous latex of a crosslinkable polydiorganosiloxane prepared by a method comprising:

(A) homogenizing a mixture comprising (1) one hundred parts by weight of a polydiorganosiloxane of the formula  $HO(R_2SiO)_xH$  wherein  $R$  is a radical selected from methyl, ethyl, propyl, phenyl, vinyl, allyl and 3,3,3-trifluoropropyl and  $x$  is an integer having an average value of three to one hundred; (2) 15-75 millimoles of surface active anionic catalyst per kilogram of polydiorganosiloxane wherein said catalyst is selected from dodecylbenzene sulfonic acid and hydrogen lauryl sulfate; and (3) water, to yield

an oil in water emulsion;

(B) admixing 0.5-15 parts by weight of an alkoxy silicon compound selected from (i) silanes of the formula  $R'_aSi(OR^3)_{4-a}$  wherein  $R'$  is a monovalent hydrocarbon radical having up to twelve carbon atoms,  $R^3$  is an alkyl radical having one to six carbon atoms and  $a$  has a value of zero or one; (ii) a partial hydrolyzate of the silane which is soluble in the polydiorganosiloxane; and (iii) mixtures of the silane and the partial hydrolyzate;

(C) maintaining the emulsion at a temperature of 15 to 30°C. for at least five hours at a pH of less than five until a crosslinked polymer emulsion is formed;

(D) admixing sufficient base to raise the pH of the crosslinked polymer emulsion to greater than seven; and optionally

(E) admixing greater than one part by weight of colloidal silica sol or colloidal silsesquioxane; to yield a latex which produces an elastomer upon removal of the water at room temperature.

2. The method according to claim 1 in which the skin care preparation is a sunscreen composition which includes as the active ingredient thereof at least one ultraviolet light absorbing compound.
3. The method according to claim 2 in which the ultraviolet light absorbing compound is 2-ethylhexyl-p-methoxycinnamate or 2-hydroxy-4-methoxybenzophenone.
4. The method according to claim 1 in which the skin care preparation is an eye cosmetic composition selected from eyebrow pencils and liquids, eye shadows, eyeliners, eye creams and mascara.
5. The method according to claim 4 in which the eye cosmetic composition is mascara which includes an active ingredient selected from waxes, oils and pigments.
6. A sunscreen preparation containing a film forming agent and at least one ultraviolet light absorbing compound as the active ingredient thereof, characterized by the film forming agent being an aqueous latex of a cross-linkable polydiorganosiloxane prepared by the method of claim 1.
7. The sunscreen preparation according to claim 6 in which the ultraviolet light absorbing compound is 2-ethylhexyl-p-methoxycinnamate or 2-hydroxy-4-methoxy-benzophenone.
8. A cosmetic containing a film forming agent, a pigment, a wax and an oil, characterized in that the film forming agent is an aqueous latex of a crosslinkable polydiorganosiloxane prepared by the method of claim 1.
9. The cosmetic according to claim 8 which is an eye cosmetic selected from eyebrow pencils and liquids, eye shadows, eyeliners, eye creams and mascara.
10. The cosmetic according to claim 8 in which the film forming agent is present in the amount of 5-20 percent by weight.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 0584

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
D, X	EP-A-0 166 396 (DOW CORNING CORPORATION) 2 January 1986 & US-A-4584341 * page 1, line 1 - line 3 * * page 4, line 24 - page 5, line 20 * * page 14, line 11 - line 20 * ---	1	A61K7/032 A61K7/48 A61K7/42 A61K7/06
A	EP-A-0 388 582 (KOBAYASHI KOSE CO LTD) 26 September 1990 * page 2, line 25 - line 36 * * page 17; example 5 * ---	4, 5, 9, 10	
A	EP-A-0 424 260 (L'OREAL) 24 April 1991 * page 18; example 11 * ---	2, 3, 6, 7	
A	EP-A-0 460 683 (DOW CORNING CORPORATION) 11 December 1991 * page 4, line 7 - page 6, line 10 * * page 8; example 11 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. CL.5)
			A61K
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		11 May 1994	Boulois, D
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

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